REMOVAL EFFICIENCY OF FLUORIDE BY La INDUCED Zr- PHOSPHATE POROUS MATERIAL

A Dissertation

Submitted in partial fulfilment for the degree of

MASTER OF SCIENCE IN CHEMISTRY

Submitted by

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410cy2021

Under The Supervision

Of

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CERTIFICATE

This is to certify that the project report entitled, **"Removal efficiency of Fluoride by La induced Zr-Phosphate porous Material",** is being submitted by **Niraj Kumar Pandey**, Roll No : **410cy2021** to the Department of Chemistry, National Institute of Technology, Rourkela, for the award of Master of Science in Chemistry is a record of bonafied research work carried out by him under my guidance and has fulfilled the requirements for the submission of thesis, which is to my knowledge has reached requisite standard.

The results contained in this dissertation have not been submitted in part or in full to any university or institute for the award or any degree.

Prof. R.K. PATEL
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I would like to thanks to all of my friends and my family members for their valuable support and encouragement.

DECLARATION

The work embodied in this report is an original investigation carried out by the author, on the topic entitled, **"**Removal efficiency of Fluoride by Lanthanum induced Zirconium phosphate porous Material**",** for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma.

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CONTENTS

ABSTRACT

The present study describes the synthesis of porous zirconium phosphate (ZrP) by incorporating Lanthanum into it for removal of fluoride from synthetic water solution. Characterization of the material was done with XRD, SEM, TG-DTA, FTIR, BET surface area, and particle size. Adsorption kinetics and isotherm of fluoride removal from aqueous synthetic solution was studied by batch model as a function of adsorbent dose, pH of solution, contact time, initial fluoride concentration and temperature. The percentage removal of fluoride was 96% at an optimal condition of initial concentration; 10mg/L, adsorbent dose; 4g/l, contact time; 120min, at pH; 7. Adsorption kinetic study revealed that the adsorption process followed pseudo-second order. The removal process followed the Langmuir adsorption isotherm. A SEM and XRD study shows that it is a porous material. The maximum loading capacity was found to be 15.55 mg/g with 100 mg/l concentration of fluoride. The process followed an endothermic nature, with variation of temp. from 20-60^{0}C. The material Lanthanum incorporated ZrP can be regenerated for further use which was tested up to five cycles of operation.

Keywords – Porous material, La-Zirconium phosphate, Fluoride adsorption

1. INTRODUCTION

One of the major environmental problems around the world is the fluoride related health hazards. More than 25 nations of the world including India suffer from the contamination of fluoride in drinking water. Orissa is one of the states where 10 out of the 30 districts is suffering from fluoride contamination. Depending on the concentration and consumption of its total amount, fluoride ions in water have beneficial as well as detrimental effects [1]. Human health is adversely affected due to the presence of fluoride in excess amount [2]. Above a certain limit, fluoride affects every living organism viz. plants, animals, humans. Fluorine is also an essential element for animals and humans. For humans, however, the essentiality has not been demonstrated unequivocally, and no data indicating the minimum nutritional requirement are available. The benefits of low fluoride dosing [3,4] and the risk of high fluoride dosing [5] have been studied.

1.1Background & Fluoride Toxicity

Fluoride is the anion F^-, the reduced form of fluorine when as an ion and when bonded to another element. Both organo fluorine compounds and inorganic fluorine containing compounds are called fluorides. Fluoride, like other halides, is a monovalent ion (-1 charge). Its compounds often have properties that are distinct relative to other halides. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxide ion.

The effects of fluoride in drinking water have been subject of research for many decades. Many epidemiological studies of possible adverse effects of the long term ingestion of fluoride via drinking water have been carried out. These studies clearly establish that fluoride primarily produces effects on skeletal tissues (bone and teeth). Low concentrations provide protection against dental carries, especially in children. This protective effect increases with concentration up to about 2 mg of fluoride per litre of drinking water.

Fluoride can also have more serious effects on skeletal tissues. Skeletal fluorosis (with adverse changes in bone structure) is observed when drinking water contains 3 mg of fluoride per litre. Crippling skeletal fluorosis develops where drinking water contains over 10 mg of fluoride per litre. The US Environmental Protection Agency considers a concentration of 4 mg/litre to be protective against crippling skeletal fluorosis.

1.2 Sources of fluoride

The following are common sources of fluoride :

(a) Fluoridated drinking water : While all of the sources mentioned below can contribute to fluoride exposure, the greatest exposure to fluoride in humans , especially in children, arises in the form of fluoridated water [1,2].

(b) Toothpaste, gels, mouthwashes, pills, other dental applications : Swallowing fluoride tablets causes dental fluorosis in 64% of young children, according to Dr. Pebbles 1974 study.

(c) Processed cereals and other foods : The act of processing foods can increase the concentrations of fluoride found in these products.

(d) Mechanically de-boned chicken : An 1999 Journal of Agriculture Food Chemistry study found that the fluoride in mechanically separated chicken contributes to the risk of dental fluorosis in children under the age of eight.

(e) Infant formula bear in mind the dangers of fluoride poisoning are particularly high in young developing children.

(f) Fish and Seafood, particularly canned fish and shell fish

(g) Foods cooked in **Teflon pans**

(h) Beer and wine, juice , soda, cigarettes

(i) Fluoridated salts

1.3Origin of fluoride

1.3.1 International

Almost all parts of the world have reported high concentration of fluoride in drinking water. North America, Africa and Asia are the mostly affected continents of the world. Countries like India, Srilanka and China have reported high concentrations of fluoride. Rift valley countries in Africa have reported high concentrations of fluoride due to the weathering of alkaline volcanic rocks.

1.3.2 India

In India, some of the groundwater sources reveal enhanced concentration of fluoride over a passage of time. This may be due to depletion of water tables and/or over withdrawal of water and/or inadequate re-charging of underground aquifer. In India 17 out of the 28 states have reported fluoride toxication results.

Fig. 1.1 : Map of India showing endemic states for fluorosis

1.4 Removal methods of fluoride

Economies followed by technology are the two restrictions in the defluoridation of drinking water. The defluoridation of drinking water is a difficult task. Here is a list of ways to obtain drinking water without fluoride.

- Membrane process
- Ion exchange process
- Adsorption method
- Co-precipitation methods

1.5 Mesostructured/Mesoporous compounds

Mesostructured - Having a structure with dimensions intermediate between micro – and macro-levels. A mesoporous material is a material containing pores with diameters between 2 and 50 nm. Porous materials are classified into several kinds by their size. According to IUPAC notation [6] microporous materials have pore diameters of less than 2 nm and macroporous materials have pore diameters of greater than 50 nm; the mesoporous category thus lies in the middle.

Typical mesoporous materials include some kinds of silica and alumina that have similarly-sized fine mesopores. Mesoporous oxides of niobium, tantalum, titanium, zirconium, cerium and tin have also been reported. The discovery of porous material has lead to a new field of research. Porous materials with large surface area, well-defined structures, also with large pores have been a new field of interest for the researchers. The basic reason for this is its limitless applications. Because of their applications in various fields Ceria and ceria based materials have earned much attention [7]. For effective improvement to the limitations of stoichiometric value A/F=14.6 [7, 8], Ce^{4+}/Ce^{3+} redox couples are subjected to use. CeO_2 is a good oxygen buffer by storing/releasing O_2.Solid-state electrolytes of solid fuel-cells [9, 10], promoters for water gas shift [11,12], supports for noble metal dispersion, and a key component of there-way catalysts (TWCs) for the elimination of toxic auto-exhaust gases [13,14] are the best examples where ceria has been applied. Mesoporous alumina–titania materials [15] have been synthesised that has wide applications. The resulting mixed metal oxides possess ordered mesopores at low to equal molar compositions of titanium in relation to aluminium (up to 50%) and worm-like mesostructures at higher molar compositions of titanium (50–75%). The structural characteristics of mixed metal oxide materials can differ greatly from that of the pure oxides. The chemical composition of these oxides has a pronounced effect on their structural, electronic and surface properties [16]. There has been great interest in obtaining well-defined mixed metal oxides with high surface area and pore volumes [17].

2. LITERATURE REVIEW

Various studies have been made related to fluoride toxicity. In amphibians like frog, it effects the development of frog embryo [18]. The fluoride toxicity effects has been seen in onions, grown in contaminated soil [19]. In GH_4C_1 pituitary tumour cell, the effects of fluoride on cell migration, cell proliferation & cell metabolism has been studied [20] & found interesting results as a future subject.

Besides living organisms, the effects of fluoride on structure & activity of NiW/Al_2O_3 catalysts for HDS of thiophene & HDN of pyridine has been studied [21]. IARC evaluated the available studies in 1987 and concluded that the limited data provide inadequate evidence of carcinogenicity in experimental animals. In a recent study in which rats and mice were given sodium fluoride in drinking-water at 11, 45, or 79 mg/litre (as fluoride ion), only the incidence of osteosarcomas in the bones of male rats increased (incidences 0/80, 0/51, 1/50, and 3/80 in the controls, low-, mid-, and high-dose groups, respectively). This increase was considered to provide equivocal evidence for a carcinogenic action in male rats; the study yielded no evidence for such an action in female rats or in male or female mice. In another recent study, no carcinogenic effect was observed in rats given sodium fluoride in the diet at dose levels of 4, 10, or 25 mg/kg of body weight per day for 2 years [22].

2.1 Defluoridation technique followed till date

The process of removal of fluoride is generally termed defluoridation. A comprehensive search of the literature reveals that following fluoride removal techniques.

Methods	Process/Material	Reference
Precipitation Co precipitation (Nalgonda Technique)	Calcium and phosphate Compounds, Aluminium salts	Dahi, 1996 [23]
Adsorption and Ion Exchange	Activated alumina	Schoeman and Steyn, 2000 [24]
	Fly ash	Chaturvedi et al., 1990 [25]
	Clays	Srimurali et al., 1998 [26]
	Soils	Omueti and Jones, 1977 [27]
	sulphonated carbonaceous materials	Mohan Rao and Bhaskaran, 1988 [28]

Membrane processes	Reverse Osmosis	Schoeman and Steyn,2000[24]
	Nanofiltration	Lhassani et al., 2001 [29]

Table. 1: Literature review

Among the various available techniques for removal of fluoride, adsorption method is relatively simple, economical and suitable for small communities [30-33].

2.2. Adsorption methods

Fluoride can be removed by adsorption onto many adsorbent materials. The criteria for selection of suitable sorbents are: cost of the medium and running costs, ease of operation, adsorption capacity, potential for reuse, number of useful cycles and the possibility of regeneration. Some of the most frequently encountered sorbents are reviewed in this section.

2.2.2. Activated alumina

Activated alumina is a granular form of aluminium. The mechanism of F^- removal from water is similar to those of a weak base ion exchange resin. Fluoride removal efficiency is excellent (typically > 95%), and is dependent on pH. Fluoride removal capacity is best in the narrow range of pH 5.5 to 6. Fine (28-48 mesh) particles of activated alumina are typically used for F^- removal. The adsorption sites on the activated alumina are also attractive to a number of anions other than F. The selectivity sequence (Johnston and Heijnen, 2002) of activated alumina in the pH range of 5.5 to 8.5 is:

$OH^- > H_2AsO_4^- > Si(OH)_3O^- > HSeO_3^- > F^- > SO_4^{2-} > CrO_4^{2-} >> HCO^{3-} > Cl^- > NO^{3-} > Br^- > I$

2.2.2. Clays and soils

The first comprehensive study of fluoride adsorption onto minerals and soils was published in 1967 (Bower and Hatcher, 1967). Since the above -mentioned paper was published, several workers studied the adsorption of fluoride. These studies include the use of Ando soils of Kenya (Zevenbergen et al., 1996), Illinois soils of USA (Omueti and Jones, 1977), Alberta soil (Luther et al., 2996), illite- goethitesoils in China (Wang and Reardon, 2001), clay pottery (Chaturvedi et al., 1988;Hauge et al., 1994), fired clay (Bardsen and Bjorvatn, 1995),

fired clay chips in Ethiopia (Moges et al., 1996), kaolinite (1997), bentonite and kaolinite (Kau et al.,1998; Srimurali et al., 1998), and fly ash (Chaturvedi et al., 1990)

2.2.3. Other sorbents

In addition to activated alumina, clays and soils other materials such as spent bleaching earth, spent catalyst, rare earth oxides, bone charcoal and activated carbon were studied as sorbents for F^-. Mahramanlioglu et al (2002) investigated the adsorption of F^- using spent bleaching earth. They found that the removal of F^- depends on the contact time, pH and adsorbent concentration. Lai and Liu (1996) studied the F^- removal from water with spent catalyst. Their findings showed that spent catalyst could be utilized as adsorbent for F^- removal. Its adsorption capacity was comparable to that of activated alumina.

Srimurali et al. (1998) investigated the removal of F^- using low cost materials such as kaolinite, bentonite, charfines, lignite and nirmali seeds. Their results show that F^- adsorption using nirmali seeds and lignite is low (6 to 8%). The removal of F^- by kaolinite is slightly better (18.2%) while charfines and bentonite give higher F^- removal capacity of 38 and 46% respectively. Chemical pretreatment was used to investigate its effect on the removal capacity of these materials. Kau et al. (1998) investigated the adsorption of F^- by kaolinite and bentonite. The results show that bentonite was found to have higher F^- adsorption than kaolinite. Chaturvedi et al. (1990) also studied the defluoridation of water by adsorption on fly ash. This study confirms their previous findings that low F^- concentration, high temperature and acidic pH favour the adsorption of F^-.

2.3. Motivation for the study

The aim of the present work was to synthesise porous Lanthanum based Zirconium phosphate and its different study for the removal of fluoride. One of the cheapest removal method was reported by Islam and Patel in 2007 [34]. Quick lime is used in this method. Removal efficiency was found to be maximum when the initial fluoride concentration was high, hence this technique of removal may be suitably employed to treat industrial effluent where the concentration of fluoride is high. But the removal of fluoride using quick lime cannot be used for domestic purpose, since it cannot bring fluoride concentration within permissible limit, and also increases the pH of the treated water. Mesostructured Zirconium phosphate [35] as an adsorbent to remove fluoride has been reported. The efficiency of the method reported 96% at a dose of 4 g/l, 120 minutes of contact time. With increase in initial fluoride

concentration, the method showed decreasing adsorption result. Another material Cerium impregnated Chitosan [41] is a low-cost efficient material which can find immense usefulness for the removal of fluoride in rural areas in a sustainable manner. Hence Lanthanum incorporated ZrP is followed to study the method with higher efficiency at higher fluoride concentration, low dosage and results at less contact time.

Lanthanum and Zirconium both have a known affinity towards fluoride. Porous Lanthanum based Zirconium phosphate represent a class of material having worth interest for evaluation of fluoride removal properties primarily because of structural characteristics of zirconium phosphate due to its meso form probably and also due to the fact of that no previous report was available regarding use of La incorporated MZrP for fluoride removal. It is further expected that structural features of the La induced ZrP could facilitate the fluoride removal in an efficient and sustainable manner

3. OBJECTIVE

- Synthesis of Lanthanum incorporated Zirconium-phosphate porous adsorbent material.
- Characterization of the synthesized material by XRD, FTIR, BET surface area and SEM.
- Evaluation of feasibility of Fluoride removal by the adsorbent material using batch adsorption process with variation of parameters like: initial fluoride concentration, adsorbent dose, pH, agitation time and temperature.
- Evaluation of the mechanism of this process by analyzing kinetics, adsorption isotherm model.
- Desorption and regeneration studies in order to know the reusability nature of adsorption.

4. EXPERIMENTAL

4.1. MATERIALS

All the reagents used in this study were of analytical grade and obtained from E. Merck, India. One litre of fluoride stock solution (1000 mg/L) was prepared, by dissolving 2.21 grams of NaF in deionised water and filling up to mark for one litre. Subsequently the stock solution was diluted with deionised water to get other subsequent concentrations as when required.

4.2. METHODS

4.2.1. Synthesis of mesostructured La-Zr phosphate

The mesoporous Zr-La phosphate was prepared using the following procedure:

Required amount of $ZrOCl_2.8H_2O$ and $La(NO_3)_3.6H_2O$ was dissolved in 100 ml of distilled water. Under stirring 3.78 g of solid $(NH_4)_2CO_3$ was added to the solution till a clear solution of zirconium carbonate complex was formed. The source of phosphate, $(NH_4)_2HPO_4$ (1.47 g) was added and dissolved into the solution. Required amount of Cetyl trimethyl ammonium bromide (CTAB) (0.61 g) was added to the solution with continuous stirring. The resultant clear solution was kept in an oven at 80^oC for 3 days in a closed polypropylene bottle for complete precipitation, which was then microwaved at 100^oC for 2 hrs. It was cooled, filtered and washed thoroughly with distilled water. The solid was collected through filtration. The solid was dried and calcined at 500^oC for 2h.

4.2.2. Characterisation

Powder XRD of the material was obtained by using PHILLIPS X''PERT X-Ray diffractometer with Cu Kα radiation (35 kV and 30 mA) over the range of $1°<2\theta<10°$ and was analyzed using standard software provided with the instrument.

Investigation of the morphology was done using JEOL JSM-6480 scanning electron microscope (acceleration voltage 15 kV). The sample was coated with platinum for 30 seconds at a current of 50 mA before the SEM micrograph was obtained.

The IR spectra of the samples were recorded (as KBr pellets) using Perkin-Elmer infrared spectrophotometer with a resolution of 4 cm^{-1} [in the range of 400-4000 cm^{-1}].

Surface area was measured by Quantasorb 1750 (Quantachrome, USA). Particle size was measured by Malvern zetasizer 6.11

The hydrogen potential at point of zero charge (pH_{PZC}) of the solid sample was determined following the under mentioned procedure. Accordingly, to a series of well-stoppered 125mL polyethylene bottles containing 40mL of 0.01 $molL^{-1}$ of KNO_3 electrolyte solution, different volumes of either 0.1 mol L^{-1} of HCl or 0.1 $molL^{-1}$ of NaOH solution were added to obtain wide ranging pH values from 1 to 10. The initial pH values (pH_i) were noted and 0.2 g of sample was added then after 72 h of equilibration at room temperature with shaking, the pH value of the supernatant liquid in each bottle was noted (pH_f). The difference between pH_i and pH_f (ΔpH) were then plotted against pH_i, the solution pH at which $\Delta pH=0$ was the pH_{PZC} of the sample.

4.2.3. Batch process

Batch adsorption were carried out by adding desired amount of adsorbent to 50 ml of the test solution in a PVC conical flask and then kept in rotatory water bath shaker. Initial fluoride concentration was kept at 10mg/L in all cases except in those, where the effect of initial fluoride concentration was to be studied. Adsorption was performed with varying the parameters like: adsorbent dose, pH, time, Initial fluoride concentration and temperature. Desorption and reusability capacities of the mesostructured material were also studied. Fluoride concentration before and after adsorption study was determined by ion selective electrode method using Orion 720 A^+ Ion analyser.

5. RESULT AND DISCUSSION

5.1. CHARACTERISATION

The PZC of the porous La-ZrP was estimated to be 6.8. Increase in the abundance of singly coordinated groups will decrease the PZC. Slightly lower PZC of the recently synthesized sample may be due to a higher fraction of singly coordinated surface groups. The BET surface area was estimated to be.423m^2/g. The particle size was found to be 186nm.

5.1.1. XRD Analysis

In fig. 5.1 three distinguishable sharp reflections that can be indexed to hkl = 100, 110, and200 for a hexagonal unit cell.

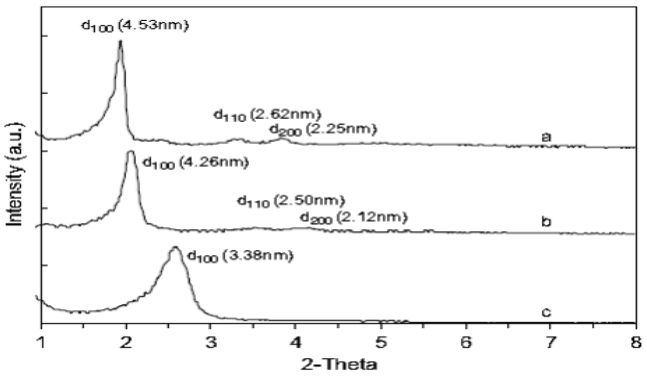

Fig. 5.1: XRD pattern (a) As synthesized, (b) Ethanol washed, (c) Calcined at 500°C

The presence of a highly intense reflection of $d_{(1\,0\,0)}$, (a=5.23nm), in as-synthesized La-ZrP is consistent with a highly ordered material with hexagonal pore structure. After ethanol wash and calcination at 500°C, the mesoporous materials still showed intensive $d_{(1\,0\,0)}$ reflections, but relatively weak $d_{(11\,0)}$ and $d_{(2\,0\,0)}$ reflections compared to as synthesized sample.

5.1.2. IR Analysis

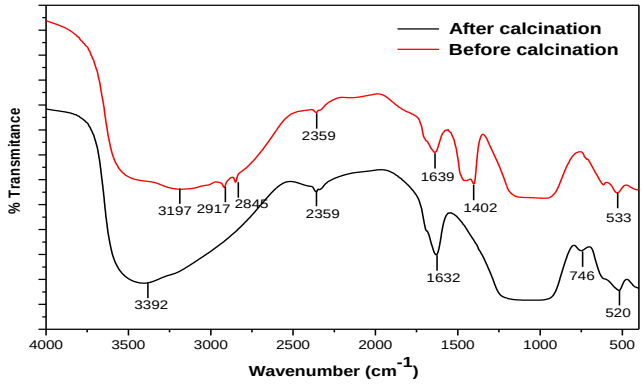

Fig. 5.2: IR spectra of La-ZrP material before and after calcination

In fig. 5.2, two sharp bands at around 2846 and 2917cm^{-1} in as synthesized La-ZrP material (before calcination), corresponds to the CH-stretching mode of the methyl group present in the surfactant ($C_{21}H_{46}BrN$) [36]. Whereas, complete disappearance of the CH-stretching band between 2800 and 3000cm^{-1} in the sample calcined at 500°C confirmed complete removal of surfactant.

5.1.3. SEM Analysis

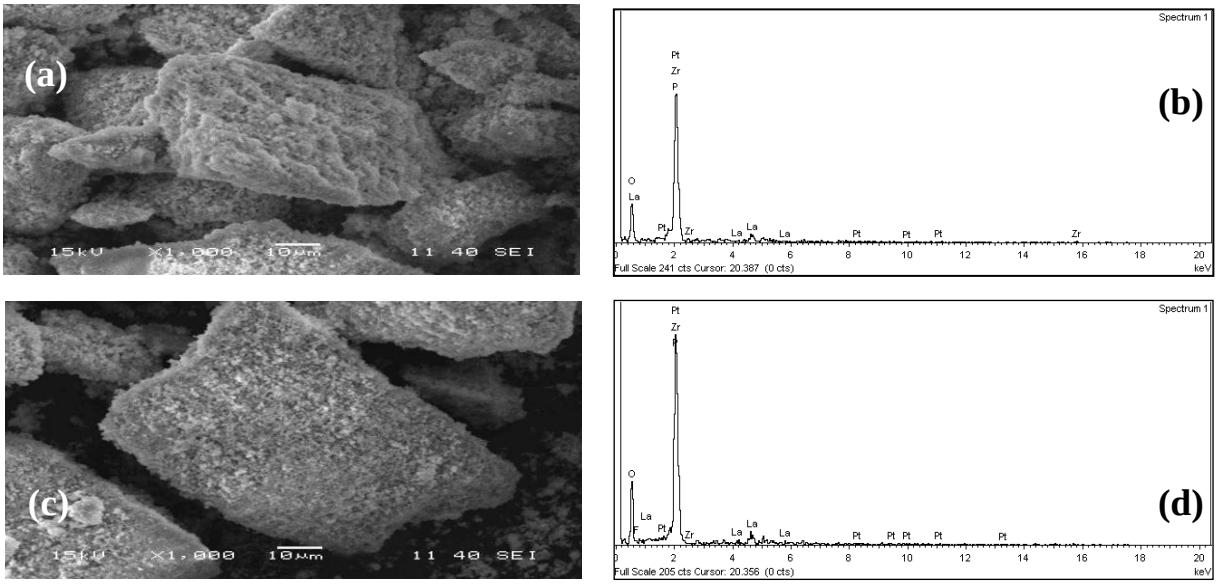

Fig. 5.3: SEM image and EDAX spectra of porous La-ZrP [(a), (b)] before adsorption, [(c), (d)] after adsorption.

The surface morphology of both Mesoporous La-ZrP (MLa-ZrP) and fluoride adsorbed (MLa-ZrP) are described in Fig. 5.3. In Fig.5.3(c) the material shows features related to agglomeration of fluoride particles compared to Fig.5.4(a).

5.2. SORPTION STUDIES

5.2.1. Effect of adsorbent dose

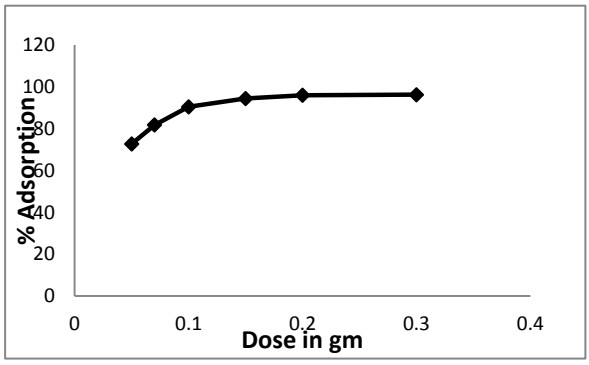

Fig. 5.4: Effect of adsorbent dose

Effect of adsorbent dose on fluoride removal was studied at ambient temperature (25 ± 2 °C) and contact time of 2 hrs for initial fluoride concentration of 10 mg/L. From Fig. 5.4, it is

evident that the removal of fluoride increased from 72.7-96.0% for 1– 6g/L of Mesoporous La-ZrP.

5.2.2. Effect of pH

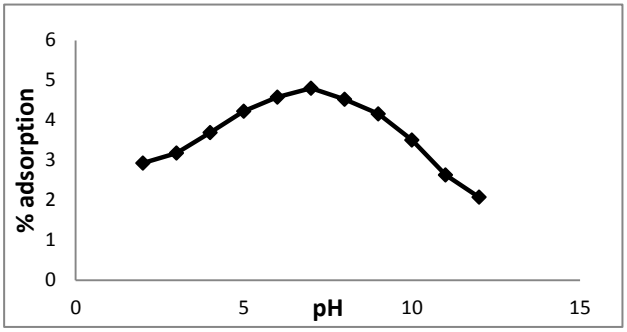

Fig. 5.5: Effect of adsorbent dose

Adsorption of fluoride by Mesostructured La-ZrP was studied in the pH range of 2–12. As shown in Fig. 5.5, the adsorption of fluoride increases within a pH range of 2–7 beyond which the adsorption decreases. The optimum removal of fluoride was found to be at pH range of 6.5–7.0.

5.2.3. Adsorption kinetics

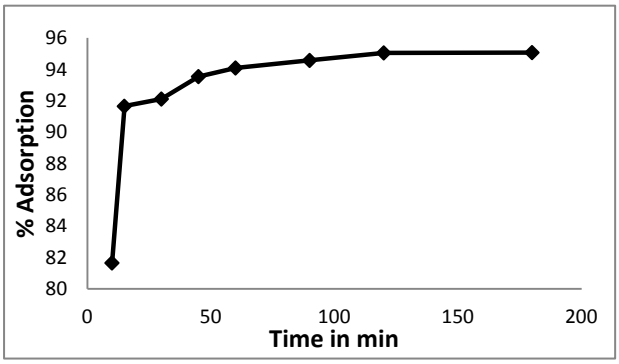

Fig. 5.6: Effect of contact time

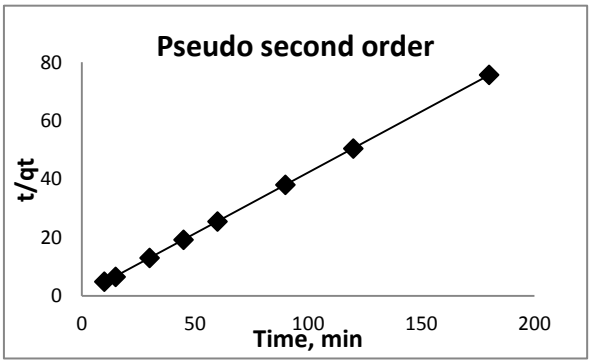

Fig. 5.7: Adsorption kinetics

The kinetics of fluoride adsorption on Mesoporous La-ZrP was verified using pseudo-first order and pseudo-second order, equation. The integrated pseudo-first order rate equation can be represented as [37]:

$$\log (q_e - q_t) = \log q_e - K_f t/2.303 \qquad (4)$$

where q_e and q_t are the amount of fluoride adsorbed (mg g^{-1}) at equilibrium and at time 't', respectively. K_f (min^{-1}) is the rate constant of pseudo-first order adsorption reaction. A straight line of log (q_e _ q_t) vs t suggests the applicability of these kinetic models. Both q_e and K_f can be determined from the intercept and slope of the curve, respectively.

The linear form of pseudo-second order kinetic model can be expressed as [38]:

$$t/q_t = 1/K_s (q_e)^2 + t/q_e \quad (5)$$

where, K_s is the rate constant for pseudo-second order reaction (g mg^{-1} min^{-1}). q_e and q_t are the amounts of solute sorbed at equilibrium and at any time 't' (mg g^{-1}), respectively. The straight line plot of t/q_t vs t for the kinetic data gives the values for q_e and K_s from the slope and intercept, respectively.

As shown in fig. 5.6, The removal amount of of fluoride increases with increase in time and finally reaches a saturation level in at 120 min where almost 96.4% of fluoride removal was achieved. Once the saturation of active sites was attained, the rate of fluoride uptake remained almost constant due to further decreases in number of available adsorbent site.

From isotherm model it was calculated that that the $q_{e,exp}$ and $q_{e,cal}$ values from the pseudo-second order kinetic model are very close to each other and the correlation coefficient R^2 found to be high (1). Therefore, the sorption kinetics can be represented by the pseudo-second order model for the adsorption fluoride onto Mesoporous La-ZrP.

5.2.4. Adsorption isotherm

Two isotherm equations have been used in the present study namely Langmuir, Freundlich isotherm models.

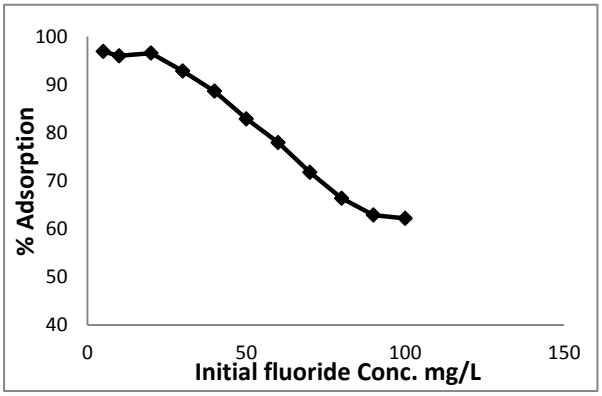

Fig. 5.8: Effect of contact time

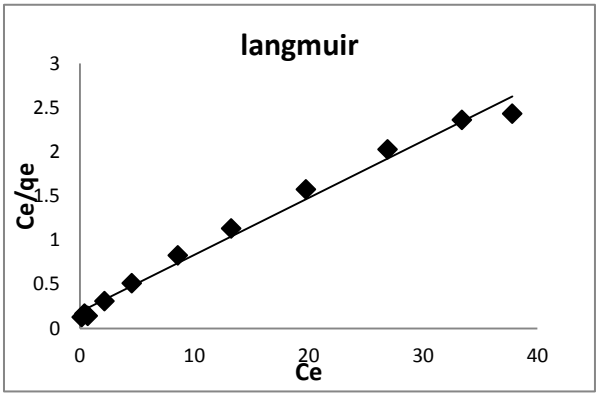

Fig. 5.9: Adsorption kinetics

The Langmuir equation can be described in the following equation [39]:

$$q_e = (q_m K_L C_e) /(1+K_L C_e) \quad (6)$$

The linearized form of Eq. (8) can be written as:

$$1/q_e = (1/K_L q_m)\,(1/C_e) + 1/q_m \qquad (7)$$

where, q_e is the amount of fluoride adsorbed at equilibrium (mg g^{-1}), Ce is the equilibrium concentration (mg L^{-1}), q_m is the mono-layer adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant related to the free adsorption energies (L mg^{-1}). The value of q_m and K_L can be calculated, respectively, from the slope and intercept of the linear plot of $1/C_e$ vs $1/q_e$.

The essential characteristics of Langmuir isotherm can be expressed as equilibrium parameter R_L[41]. Thus, R_L can be expressed as:

$$R_L = 1/(1+K_L C_o) \qquad (18)$$

where, C_o is the initial concentration of fluoride (mg L^{-1}). In this results of fig, 5.10, the value of R_L for the initial fluoride concentration of 100 mg $L^{-1}$was found to be 0.0644 indicating a favourable condition of adsorption of fluoride and the value of q_m was found to be 2.953.

5.2.5. Effect of temperature

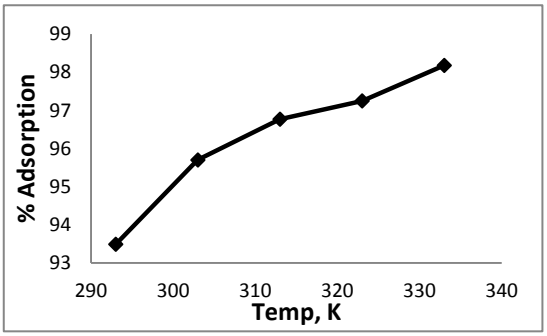

Fig. 5.10: Effect of temperature

The effect of temperature on the adsorption of fluoride with initial concentration 10 mg/L, examined is represented in fig. 5.10. as percentage removal of fluoride versus temperature. The percentage removal of fluoride with initial concentration 10 mg/L, increased from 93.4 – 98.1%, for 20°C – 60°C temperature. The continuous increase in percentage removal with temperature indicated that the adsorption process was endothermic in nature.

5.2.6. Regeneration and reuse studies

Desorption studies were carried out by using fluoride adsorbed Mesoporous La-ZrP with variation of pH of the medium. The results of the desorption study are shown in fig. 5.11. Leaching of fluoride from the adsorbent material was negligible in acidic pH of the medium.

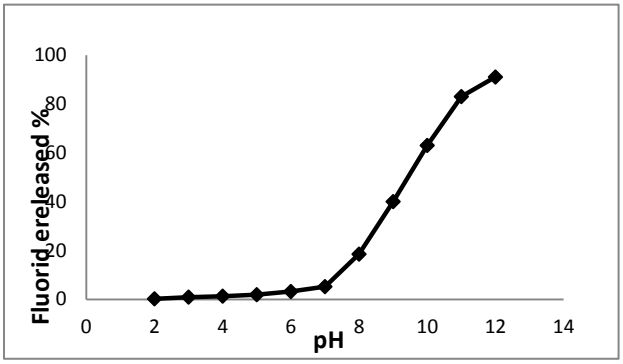

Fig. 5.11: Desorption study

However in alkaline pH (pH > 8), substantial amount of fluoride could be eluted out and subsequently nearly 91% of the fluoride could be leached from the adsorbent material at pH=12. The regenerated material can be used successfully for a number of continuous cycles of operation in a batch technique.

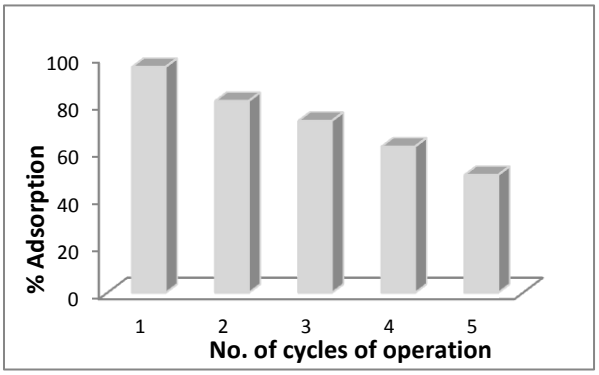

Fig. 5.12: Bar diagram showing the percentage of removal of fluoride in different cycle of batch operation.

Effective reuse of adsorbent material directly affects the cost factor and hence its utility in continuous batch adsorption processes for further defluoridation. The reusability capacity was performed with dried adsorbent. As shown in Fig. 5.12, the percentage of adsorption of fluoride by Mesoporous La-ZrP was found to be reduced from 95.5 to 49.8 % following a sequence of 1st to 5th cycle of batch operation study.

6. CONCLUSION

In the present study a novel adsorbent material (Mesoporous La-ZrP) was prepared which was successfully utilized for the removal of fluoride from synthetic water solution. Some of the important conclusions of the study are

- Maximum fluoride could be removed at solution pH 7.0,
- The adsorption process followed a pseudo-second order kinetic model.
- Langmuir isotherm model is the most suitable model to satisfactorily describe the adsorption phenomenon.
- The removal at all temperature confirms the spontaneous nature of sorption process of fluoride with an endothermic nature of process.
- Desorption study indicated that the material can be conveniently regenerated and reused for the removal of fluoride.
- The synthesized material is a low-cost efficient material which can be used for the removal of fluoride in rural areas
-

7. FUTURE WORK

- ❖ Characterisation of the sample by TEM, Porosity meter and to measure the pore size and pore depth of the material.
- ❖ Investigation of effect of other Compettitive anions and ermoval efficiency of fluoride with ground water sample.
- ❖ Design of a model incorporating the results of fluoride adsorption and kinetic studies of the removal process.
- ❖ Column studies on the removal efficiency of Fluoride.

8. REFERENCE

[1] E.J. Underwood, *Trace Elements in Human and Animal Nutrition, Academic Press, New York,* **1997**, 545.

[2] WHO, Fluorine and Fluorides, Environmental Health Criteria, WHO, Geneva, 36, **1984**.

[3] A.K. Susheela;*Treatise on Fluorosis, Fluorosis Research and Rural Development Foundation, India,* **2001**.

[4] K.C. Agarwal, S.K. Gupta, A.B. Gupta; *Water Sci. Technol*. 40 (**1999**) 167.

[5] M. Hichour, F. Persin, J. Sandeaux, C. Gavach; *Sep. Purif. Technol.* 18 (**2000**) 1–11.

[6] J. P. Arenas, M. J. Crocker;*Pure & Appl. Chem,* 66 (**1994**) 1739-1758.

[7] K. C.Taylor; *Catalysis Reviews: Science and Engineering*, 35 (**1993**) 457.

[8] K. C. Taylor, J. R. Anderson, M. Boudart,;*Catalysis-Science and Technology. Berlin, Springer-Verlag*, **1984**.

[9] E. P. Murray, T. Tsai, S. A. Barnett; *A.Nature,* 400 **(1999**) 649.

[10] Z. P. Shao, S. M. Haile. *Nature*, 431 (**2004**) 170.

[11] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos ; *Science*, 301 **(2003**) 935.

[12] W. L. Deng, M. Flytzani-Stephanopoulos; *Angew. Chem. Int. Ed*., 45 (**2006**) 2285.

[13] J. R. Gonzalez-Velasco, M. A. Gutierrez-Ortiz, J. L. Marc, J. A. Botas, M. P. Gonzalez-Marcos, G. Blanchard; *Appl. Catal. B: Environmental*, **22**(**1999**) 167.

[14] S. Letichevsky, C. Z. Tellez, R. R. de Avillez, M. I. P. de Silva, M. A. Fraga, L. G. Appel; *Appl. Catal.B: Environmental,* 58 (**2005**) 203.

[15] S. M. Morris , J. A. Horton , M. Jaroniec; *Microporous and Mesoporous Materials,* 128 (2010) 180–186.

[16] J.A. Rodriguez, M. Fernandez-Garcia; *John Wiley and Sons, Hoboken*, NJ, **2007**.

[17] J. Cejka; *Appl. Catal. A,* 254 (**2003**) 327.

[18] E.H. Goh, A.W. Neh; *Food and Chemical Toxicology,*41(**2003**)1501–1508.

[19] S.K Jha, A.K Nayak, Y.K Sharma; *Chemosphere* 76 (**2009**) 353–356.

[20] A. Mendoza-Schulz, E. Solano-Agama; *Toxicology Letters*, 190 (**2009**) 179-186.

[21] A. Benitez, J. Ramfrez, J.L. G. Fierro, A.L. Agudo; *Applied Catalysis A: General*, 144 (**1996**) 343-364.

[22] Kanbur, G. Eraslan; *Food and chemical toxicology*, 17 (**2009**) 1184-1189.

[23] E. Dahi, F. Mtalo, B. Njau, H. Bregnhj; 22nd*WEDC Conference,* New Delhi, India, **1996**.

[24] J. J. Schoeman, A. Steyn; Defluoridation, denitrification and desalination of water using ion-exchange and reverse osmosis technology. Water Research Commission, Pretoria. ISBN: 1 86845 597 1 (**2000**).

[25] A. K. Chaturvedi, K.P. Yadav, K. C. Pathak, V. N.; *Water, Air, Soil Pollut.,* 49 (**1990**) 51-61.

[26] M. Srimurali, A. Pragathi, J. Karthikeyan; *Environmental Pollution,* 99 (**1998**) 285-289.

[27] J. A. I. Omueti, R. L. Jones; Journal of Soil Science, 28 (**1977**) 564-572.

[28] N. V. R. Mohan Rao, C.S. Bhaskaran; Journal of fluorine Chemistry, 41 (**1988**) 17-24.

[29] A. Lhassani, M. Rumeau, D. Benjelloun, M. Pontié, *Wat. Res*., 35 (**2001**)3260–3264.

[30] M. Mohapatra, S. Anand, B.K. Mishra, D.E. Giles, P. Singh; J. *Environ. Manage,* 91 (**2009**) 67–77.

[31] Y. Tang, J. Wang, N. Gao; *J. Environ. Sci.*, 22 (**2010**) 1689–1694.

[32] N. Viswanathan, S. Meenakshi,; *Appl. Clay Sci.,* 48 (**2010**) 607–611.

[33] V. Khatibikamal, A. Torabian, F. Janpoor, G. Hoshyaripour; *J. Hazard. Mater.*,179 (**2010**) 276–280.

[34] M. Islam, R.K. Patel; *Journal of Hazardous Material,* 143 (**2007**) 303-310.

[35] S. K. Swain, T. Patnaik, B. K. Singh, U. Jha, R. K. Patel, A.K. Dey, *Chemical engineering journal,* 171 (**2011**) 1218-1226.

[36] Y. Xi, Z.Ding, H.He, R.L. Frost; *Spectrochim. Acta A.*, 61 (**2005**) 515–525.

[37] B. Pihlar, Z. Cencic; *Anal. Chim. Acta,* 273 (**1993**) 267–274.

[38] R.K. Dey, U. Jha, A.C. Singh, S. Samal and A.R. Ray; *Anal. Sci.,* 8 (**2006**) 1105-110.

[39] S.J. Allen, G. Mckay and J.F. Porter; J. *Colloid Interface Sci.*, 280 (**2004**) 322-333.

[40] S.K. Swain, T. Padhi, T. Patnaik, R.K. Patel, U. Jha, R.K. Dey; *Desalination Water Treat.,* 13 (**2010**) 369–381.